The Preparation and Crystal Structure of *trans*-Bis(sulphinylnitrilo)-bis(triphenylphosphine)platinum(II): *trans*-[Pt(NSO)$_2$(PPh$_3$)$_2$]

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Reaction of (η^2-ethene)bis(triphenylphosphine)platinum(0) with Hg(NSO)$_2$ yields *trans*-bis(sulphinylnitrilo)-bis(triphenylphosphine)platinum-(II); the NSO$^-$ ligands are σ-bonded.

Currently there are relatively few examples of transition metal complexes containing sulphur–nitrogen ligands[1] although it is clear that reactive S–N fragments may be stabilised by metal centres. We are involved in the synthesis of compounds with two goals. Firstly, the preparation of materials which have interesting solid state properties[2] and secondly the synthesis of complexes containing small NS ligands which are isoelectronic with more well known groups. We have recently reported[3] on the preparation of *cis*-Pt(NSNSiMe$_3$)$_2$(PPh$_3$)$_2$ which contains the $^-$NSNSiMe$_3$ ligand (isoelectronic with SO$_2$). Herein we report that reaction of Hg(NSO)$_2$ with (η^2-ethene)bis(tri-phenylphosphine)platinum(0) yields *trans*-Pt(NSO)$_2$(PPh$_3$)$_2$. There has only previously been one authenticated report[4] of the preparation of an NSO$^-$ complex (for rhodium) and this compound was prepared using CsNSO$_2$ whereas the method reported here, equation (1), is rational.

$$\mathrm{Pt(C_2H_4)(PPh_3)_2 + Hg(NSO)_2 \rightarrow Pt(NSO)_2(PPh_3)_2 + Hg + C_2H_4} \quad (1)$$

In a typical experiment Pt(C$_2$H$_4$)(PPh$_3$)$_2$ (0.15 mmol) was added to a solution of Hg(NSO)$_2$ (0.15 mmol) in 10 cm^3 of tetrahydrofuran (THF). After stirring for 2 hours the reaction

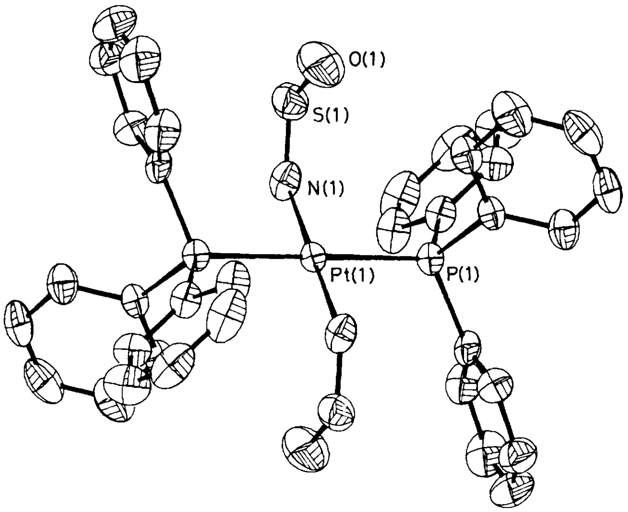

Figure 1. The molecular structure of *trans*-Pt(NSO)$_2$(PPh$_3$)$_2$. Selected bond distances and angles are: Pt(1)–P(1) 2.328(3), Pt(1)–N(1) 1.994(6), N(1)–S(1) 1.472(7), S(1)–O(1) 1.455(8) Å, P(1)–Pt–N(1) 92.0(3), Pt–N(1)–S(1) 133.3(4), N(1)–S(1)–O(1) 120.7(5)°.

mixture was reduced to dryness and extracted with 10 cm^3 of benzene. Concentration of this solution and addition of hexane gave the product (0.6 mmol). Yellow crystals suitable for *X*-ray analysis† were obtained from benzene–hexane. Satisfactory C, H, and N microanalyses were obtained whilst $^{31}P\{^1H\}$ n.m.r. spectroscopy (C_6D_6) gave a 1:4:1 triplet, δ 19.03 p.p.m., ^1J(Pt–P) 2854 Hz. I.r. $\nu_{as.}$(NSO) 1218(s), $\nu_{sym.}$(NSO) 1099(s), δ(NSO) 590(w) cm^{-1}.

The structure of the molecule is shown in Figure 1. As expected from the Pt–P coupling constant the complex is square planar with Pt–P distances which are appropriate for Pt^{II}. The anionic NSO^- ligands are σ-bonded to the platinum but from the n.m.r. studies it is not possible to distinguish N or O co-ordination. The crystallographic studies, however suggest that co-ordination *via* nitrogen occurs. The S–N and S–O distances do not differ significantly from each other, indicate double bonds, and are slightly shorter than those observed in $Pt(NSNSiMe_3)_2(PPh_3)_2$. A surprising feature of the reaction is the formation of the *trans* isomer. Reaction of *cis*-$PtCl_2(PR_3)_2$ with $Hg(NSO)_2$ proceeds cleanly by $^{31}P\{^1H\}$ n.m.r. spectroscopy (for $PR_3 = PPh_3$, δ 8.12 p.p.m., ^1J(Pt–P) 3257 Hz) to give what we assume is the *cis* isomer but, to date, we have been unable to isolate pure material.

The NSO^- ligand is isoelectronic with SO_2; however the co-ordination mode reported here is not observed for SO_2; doubtless numerous examples of NSO^- complexes are available and transmetallation reactions using $Hg(NSO)_2$ would appear to be a facile route.

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† *Crystal data:* $C_{36}H_{30}N_2O_2P_2S_2Pt$, M = 843.78, monoclinic, a = 9.427(1), b = 20.123(3), c = 9.746(19) Å, β = 67.84(1)°, U = 1712 $Å^3$, space group $P2_1/n$, Z = 2, D_c = 1.636 g cm^{-3}, Mo-K_α radiation, λ = 0.71069 Å, μ(Mo-K_α) = 41.5 cm^{-1}, $F(000)$ = 832. R = 0.0317, R_w = 0.0264 for 1961 observed [$I > 1.5\sigma(I)$] diffractometer reflections out of 3011 measured (h 0 − 11, k 0 − 23, l 0 ± 11, $1.5 \leqslant 8 \leqslant 25°$) and corrected for absorption empirically. The μ_{iso} values for N and O for the structure as presented are 0.053 and 0.122; for the alternative possibility of Pt–O bonding the μ_{iso} values for N and O were 0.076 and 0.088 with the R value being 0.0322 (R_w = 0.0272). Although numerically the μ_{iso} values tend to indicate a preference for the alternative arrangement we are prepared to accept that proposed because: (a) the N μ_{iso} is closer to that of Pt, to which it is bonded, (b) the oxygen atom is quite likely to be undergoing significant thermal motion, as indeed the sulphur atom appears to be, and (c) the R values for the proposed arrangement are lower. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. Notice to Authors, Issue No. 1.